



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US89/04674 <b>(22) International Filing Date:</b> 23 October 1989 (23.10.89) <b>(30) Priority data:</b> 282,072 7 December 1988 (07.12.88) US <b>(71) Applicant:</b> HUGHES AIRCRAFT COMPANY [US/US]; 7200 Hughes Terrace, Los Angeles, CA 90045-0066 (US). <b>(72) Inventors:</b> JACKSON, David, P. ; 22328 W. Barcotta Drive, Saugus, CA 91350 (US). BUCK, Orval, F. ; 2435 25th Street, Santa Monica, CA 90405 (US). <b>(74) Agents:</b> LACHMAN, Mary, E. et al.; Hughes Aircraft Company, P.O. Box 45066, Bldg. C1, M.S. A126, Los Angeles, CA 90045-0066 (US).		<b>(81) Designated States:</b> AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK, FR (European patent), GB (European patent), IT (European patent), LU (European patent), NL (European patent), NO, SE (European patent).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> CLEANING PROCESS USING PHASE SHIFTING OF DENSE PHASE GASES  <b>(57) Abstract</b>  A process for removing two or more contaminants from a substrate in a single process. The substrate to be cleaned is contacted with a dense phase gas at or above the critical pressure thereof. The phase of the dense phase gas is then shifted between the liquid state and the supercritical state by varying the temperature of the dense fluid in a series of steps between temperatures above and below the critical temperature of the dense fluid. After completion of each step in the temperature change, the temperature is maintained for a predetermined period of time in order to allow contact with the substrate and contaminants and removal of the contaminants. At each step in the temperature change, the dense phase gas possesses different cohesive energy density or solubility properties. Thus, this phase shifting of the dense fluid provides removal of a variety of contaminants from the substrate without the necessity of utilizing different solvents. In alternative embodiments, ultraviolet radiation, ultrasonic energy, or reactive dense phase gas or additives may additionally be used.		

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CLEANING PROCESS  
USING PHASE SHIFTING OF  
DENSE PHASE GASES

1

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates generally to the use of dense phase gases for cleaning substrates. More particularly, the present invention relates to a process utilizing phase shifting of dense phase gases or gas mixtures in order to enhance the cleaning of a wide  
10 variety of substrates, including complex materials and hardware.

2. Description of Related Art

15 Conventional solvent-aided cleaning processes are currently being re-evaluated due to problems with air pollution and ozone depletion. In addition, recent environmental legislation mandates that many of the organic solvents used in these processes be banned or their use severely limited. The use of dense phase gases  
20 or gas mixtures for cleaning a wide variety of materials has been under investigation as an alternative to the above-mentioned solvent-based cleaning processes. A dense phase gas is a gas compressed to either supercritical or subcritical conditions to achieve liquid-like densities.  
25 These dense phase gases or gas mixtures are also referred

1 to as dense fluids. Unlike organic solvents, such as  
n-hexane or 1,1,1-trichloroethane, dense fluids exhibit  
unique physical and chemical properties such as low  
5 surface tension, low viscosity, and variable solute  
carrying capacity.

The solvent properties of compressed gases is well  
known. In the late 1800's, Hannay and Hogarth found that  
inorganic salts could be dissolved in supercritical  
ethanol and ether (J. B. Hannay and H. Hogarth,  
10 J.Proc.Roy.Soc. (London), 29, p. 324, 1897). By the early  
1900's, Buchner discovered that the solubility of organics  
such as naphthalene and phenols in supercritical carbon  
dioxide increased with pressure (E. A. Buchner,  
Z.Physik.Chem., 54, p. 665, 1906). Within forty years  
15 Francis had established a large solubility database for  
liquified carbon dioxide which showed that many organic  
compounds were completely miscible (A. W. Francis,  
J.Phys.Chem., 58, p. 1099, 1954).

In the 1960's there was much research and use of dense  
20 phase gases in the area of chromatography. Supercritical  
fluids (SCF) were used as the mobile phase in separating  
non-volatile chemicals (S. R. Springston and M. Novotny,  
"Kinetic Optimization of Capillary Super-critical  
Chromatography using Carbon Dioxide as the Mobile Phase",  
25 CHROMATOGRAPHIA, Vol. 14, No. 12, p. 679, December 1981).  
Today the environmental risks and costs associated with  
conventional solvent-aided separation processes require  
industry to develop safer and more cost-effective  
alternatives. The volume of current literature on  
30 solvent-aided separation processes using dense carbon  
dioxide as a solvent is evidence of the extent of  
industrial research and development in the field.  
Documented industrial applications utilizing dense fluids  
include extraction of oil from soybeans (J. P. Friedrich  
35 and G. R. List and A. J. Heakin, "Petroleum-Free Extracts

1 of Oil from Soybeans", JAOCS, Vol. 59, No. 7, July 1982),  
decaffination of coffee (C. Grimmett, Chem. Ind., Vol. 6,  
p. 228, 1981), extraction of pyridines from coal  
(T. G. Squires, et al, "Super-critical Solvents. Carbon  
5 Dioxide Extraction of Retained Pyridine from Pyridine  
Extracts of Coal", FUEL, Vol. 61, November 1982),  
extraction of flavorants from hops (R. Vollbrecht,  
"Extraction of Hops with Supercritical Carbon Dioxide",  
Chemistry and Industry, 19 June 1982), and regenerating  
10 absorbents (activated carbon) (M. Modell, "Process for  
Regenerating Absorbents with Supercritical Fluids", United  
States Patent No. 4,124,528, 7 November 1978).

Electro-optical devices, lasers and spacecraft  
assemblies are fabricated from many different types of  
15 materials having various internal and external geometrical  
structures which are generally contaminated with more than  
one type of contamination. These highly complex and  
delicate assemblies can be classified together as "complex  
hardware". Conventional cleaning techniques for removing  
20 contamination from complex hardware require cleaning at  
each stage of assembly. In addition to the above-  
mentioned problems with conventional solvent-aided  
cleaning techniques, there is also a problem of  
recontamination of the complex hardware at any stage  
25 during the assembly process. Such recontamination  
requires disassembly, cleaning, and reassembly.  
Accordingly, there is a present need to provide  
alternative cleaning processes which are suitable for use  
in removing more than one type of contamination from  
30 complex hardware in a single process.

#### SUMMARY OF THE INVENTION

35 In accordance with the present invention, a cleaning  
process is provided which is capable of removing different

1 types of contamination from a substrate in a single  
process. The process is especially well-suited for  
removing contaminants such as oils, grease, flux residues  
and particulates from complex hardware.

5 The present invention is based on a process wherein  
the substrate to be cleaned is contacted with a dense  
phase gas at a pressure equal to or above the critical  
pressure of the dense phase gas. The phase of the dense  
phase gas is then shifted between the liquid state and the  
10 supercritical state by varying the temperature of the  
dense fluid in a series of steps between temperatures  
above and below the critical temperature of the dense  
fluid. After completion of each step in the temperature  
change, the temperature is maintained for a predetermined  
15 period of time in order to allow contact with the  
substrate and contaminants and removal of the  
contaminants. At each step in the temperature change, the  
dense phase gas possesses different cohesive energy  
density or solubility properties. Thus, this phase  
20 shifting of the dense fluid provides removal of a variety  
of contaminants from the substrate without the necessity  
of utilizing different solvents.

In an alternative embodiment of the present invention,  
the cleaning or decontamination process is further  
25 enhanced by exposing the dense phase gas to ultraviolet  
(UV) radiation during the cleaning process. The UV  
radiation excites certain dense phase gas molecules to  
increase their contaminant-removal capability.

In another alternative embodiment of the present  
30 invention ultrasonic energy is applied during the cleaning  
process. The ultrasonic energy agitates the dense phase  
gas and substrate surface to provide enhanced  
contamination removal.

In yet another alternative embodiment of the present  
35 invention, a dense phase gas which reacts with the  
contaminants is used to enhance contaminant removal.

1       The above-discussed and many other features and  
attendant advantages of the present invention will become  
better understood by reference to the following detailed  
description when considered in conjunction with the  
5       accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawings:

10       FIG. 1 presents a phase diagram for a preferred  
exemplary dense phase gas in accordance with the present  
invention, and a corresponding curve of cohesive energy  
versus temperature.

15       FIG. 2 is a diagram illustrating an exemplary  
temperature cycling sequence used to produce the phase  
shifting in accordance with the present invention.

FIG. 3 is a flowchart setting forth the steps in an  
exemplary process in accordance with the present invention.

20       FIG. 4 is a diagram of an exemplary system for use in  
accordance with the present invention.

FIG. 5a and FIG. 5b are schematic diagrams of  
exemplary racks used to load and hold the substrates to be  
cleaned in accordance with the present process.

25       FIG. 6 is a partial sectional view of a preferred  
exemplary cleaning vessel for use in accordance with a  
first embodiment of the present invention.

FIG. 7 is an alternate exemplary cleaning vessel in  
accordance with a second embodiment of the present  
invention using multi-phase dense fluid cleaning.

30       FIG. 8 is an alternative exemplary cleaning vessel in  
accordance with a third embodiment of the present  
invention for use in applying sonic energy during cleaning.

35       FIGS. 9a and 9b show an alternate exemplary cleaning  
vessel for use in applying radiation to the dense phase  
gas during the cleaning process of fourth and fifth  
embodiments of the present invention.

1                    DESCRIPTION OF THE PREFERRED EMBODIMENTS

5                    The dense phase fluids which may be used in accordance  
with the present invention include any of the known gases  
which may be converted to supercritical fluids or liquified  
at temperatures and pressures which will not degrade the  
physical or chemical properties of the substrate being  
cleaned. These gases typically include, but are not  
limited to: (1) hydrocarbons, such as methane, ethane,  
10                   propane, butane, pentane, hexane, ethylene, and propylene;  
(2) halogenated hydrocarbons such as tetrafluoromethane,  
chlorodifluoromethane, sulfur hexafluoride, and  
perfluoropropane; (3) inorganics such as carbon dioxide,  
ammonia, helium, krypton, argon, and nitrous oxide; and  
15                   (4) mixtures thereof. The term "dense phase gas" as used  
herein is intended to include mixtures of such dense phase  
gases. The dense phase gas selected to remove a  
particular contaminant is chosen to have a solubility  
chemistry which is similar to that of the targeted  
20                   contaminant. For example, if hydrogen bonding makes a  
significant contribution to the internal cohesive energy  
content, or stability, of a contaminant, the chosen dense  
phase gas must possess at least moderate hydrogen bonding  
ability in order for solvation to occur. In some cases, a  
25                   mixture of two or more dense phase gases may be formulated  
in order to have the desired solvent properties, as  
discussed hereinbelow with regard to an alternative  
embodiment of this invention. The selected dense phase  
gas must also be compatible with the substrate being  
30                   cleaned, and preferably has a low cost and high health and  
safety ratings.

                  Carbon dioxide is a preferred dense phase gas for use  
in practicing the present invention since it is  
inexpensive and non-toxic. The critical temperature of  
35                   carbon dioxide is 305° Kelvin (32°C) and the critical



1 pressure is 72.9 atmospheres. The phase diagram for  
carbon dioxide is set forth in FIG. 1. At pressures above  
the critical point, the phase of the carbon dioxide can be  
5 shifted between the liquid phase and supercritical fluid  
phase by varying the temperature above or below the  
critical temperature of 305 Kelvin (K).

In accordance with the present invention, a single  
dense phase gas or gas mixture is phase shifted in order  
to provide a spectrum of solvents which are capable of  
10 removing a variety of contaminants. "Phase shifting" is  
used herein to mean a shift between the liquid state and  
the supercritical state as represented by the bold  
embodiment of this invention. The selected dense phase  
arrow 10 in FIG. 1. The phase shifting is accomplished by  
15 varying the temperature of the dense phase gas while  
maintaining the pressure at a relatively constant level  
which is at or above the critical pressure of the dense  
phase gas. The pressure is predetermined by computation  
to provide the necessary solvent spectrum during  
20 temperature cycling, as described in greater detail  
hereinbelow. The temperature of the dense phase gas is  
varied in a series of steps between a temperature above  
the critical temperature of the dense phase gas and a  
temperature below this critical temperature. As indicated  
25 in curve 12 in FIG. 1, this temperature change produces a  
change in the cohesive energy density or solubility  
parameter of the dense phase gas. As shown in FIG. 1,  
increasing the temperature of dense phase carbon dioxide  
from 300K to 320K changes the gas solvent cohesive energy  
30 content from approximately 24 megapascals<sup>1/2</sup> (MPa<sup>1/2</sup>) to  
12 MPa<sup>1/2</sup>. This change in cohesive energy content produces  
a change in the solvent properties of the dense phase  
gas. Thus, in accordance with the present invention, the  
solvent properties of the dense phase gas may be  
35 controlled in order to produce a variation in solvent

1 properties such that the dense phase gas is capable of  
dissolving or removing a variety of contaminants of  
differing chemical composition in a single treatment  
process. A spectrum of distinct solvents is provided from  
5 a single dense phase gas or gas mixture. The cohesive  
energy of the dense phase gas is matched to that of the  
contaminant in order to remove the contaminant.

Optionally, the cohesive energy of the dense phase gas is  
also matched to that of the substrate in order to produce  
10 substrate swelling, as discussed in further detail below.

The phase shifting is accomplished in accordance with  
the present invention by a step-wise change in  
temperature, as indicated by way of example in FIG. 2,  
where  $T$  is the process or operating temperature and  $T_c$   
15 is the critical temperature. In FIG. 2, at a constant  
pressure greater than the critical pressure, the  
temperature is incrementally decreased to a point below  
 $T_c$  and is then incrementally increased to the starting  
temperature above  $T_c$ . After each step in the  
20 temperature change, the temperature is held constant for a  
predetermined period of time during which the substrate  
and contaminants are exposed to the dense phase gas and  
contaminants are removed. As discussed with regard to  
FIG. 1, at each step in the temperature change of FIG. 2,  
25 the dense phase gas has different solvent properties,  
i.e., a different solvent exists at each step.

Consequently, a variety of contaminants can be removed by  
this solvent spectrum. The stepwise change from  $T > T_c$  to  
 $T < T_c$  and back to  $T > T_c$  is referred to herein as a  
30 "temperature cycle." The starting point for the  
temperature cycling maybe either above or below the  
critical temperature. In accordance with the present  
process, the temperature cycle may be repeated several  
times, if required, in order to produce increased levels

1 of contaminant removal. Each successive cycle removes  
more contaminants. For example after one cycle, 30  
percent of the contaminants may be removed; after the  
second cycle, 60 percent of the contaminants may be  
5 removed; and after the third cycle, 75 percent of the  
contaminants may be removed. The phase shift cycle of the  
present invention also improves contaminant removal by  
enhancing floatation and inter-phase transfer of  
contaminants, thermally-aided separation of contaminants,  
10 and micro-bubble formation.

The values of operating temperature and pressure used  
in practicing the process of the present invention may be  
calculated as follows. First, the cohesive energy value  
of the contaminants is computed or a solubility value is  
15 obtained from published data. Next, based upon the  
critical temperature and pressure data of the selected  
dense phase gas or gas mixture, and using gas solvent  
equations, such as those of Giddings, Hildebrand, and  
others, a set of pressure/temperature values is computed.  
20 Then, a set of curves of solubility parameter versus  
temperature is generated for various pressures of the  
dense phase gas. From these curves, a phase shift  
temperature range at a chosen pressure can be determined  
which brackets the cohesive energies (or solubility  
25 parameters) of the contaminants. Due to the complexity of  
these calculations and analyses, they are best  
accomplished by means of a computer and associated  
software.

The number of times the phase shift cycle is repeated,  
30 the amount of change in temperature for each step in the  
cycle, and the residence time at each step are all  
dependent upon the extent of contaminant removal which is  
required, and can readily be determined experimentally as  
follows. The substrate is subjected to one or more phase  
35 shift cycles in accordance with the present invention, and  
then the substrate is examined to determine the extent of

1 cleaning which has been accomplished. The substrate may  
be examined by visual or microscopic means or by testing,  
such as according to the American Society for Testing and  
Materials, Standard E595 "Total Mass Loss (TML) and  
5 Collected Volatile Condensable Material (CVCM)."  
Depending on the results obtained, selected process  
parameters may be varied and their effect on the extent of  
contaminant removal determined. From this data, the  
optimum process parameters for the particular cleaning  
10 requirements may be determined. Alternatively, the  
exhausted gas solvent may be analyzed to determine the  
amount of contaminants contained therein. Gravimetric,  
spectroscopic, or chromatographic analysis may be used for  
this purpose. The extent of contaminant removal is then  
15 correlated with the various process parameters to  
determine the optimum conditions to be used. Typical  
process parameters which have been found to be useful  
include, but are not limited to, the following: variation  
of the temperature above the critical temperature by about  
20 5 to 100K; variation of the temperature below the critical  
temperature by about 5 to 25K; step changes in temperature  
of about 5 to 10K; and residence time at each step of  
about 5 to 30 minutes.

25 A flowchart showing the steps in the cleaning process  
of a first embodiment of the present invention is  
presented in FIG. 3. The process is carried out in a  
cleaning vessel which contains the substrate to be  
cleaned. Various exemplary cleaning vessels will be  
described in detail below. As shown in FIG. 3, the  
30 cleaning vessel is initially purged with an inert gas or  
the gas or gas mixture to be used in the cleaning  
process. The temperature in the pressure vessel is then  
adjusted to a temperature either below the critical  
temperature (subcritical) for the gas or gas mixture or  
35 above or equal to the critical temperature (supercritical)

1 for the gas. The cleaning vessel is next pressurized to a  
pressure which is greater than or equal to the critical  
pressure for the gas or gas mixture. At this point, the  
gas is in the form of a dense fluid. The phase of this  
5 dense fluid is then shifted between liquid and  
supercritical states, as previously described, by varying  
the temperature over a predetermined range above and below  
the critical point, as determined by the type and amount  
of contaminants to be removed. Control of temperature,  
10 pressure and gas flow rates is best accomplished under  
computer control using known methods.

The process of controlled temperature variation to  
achieve phase shifting has been discussed with regard to  
FIG. 2. Phase shifting back and forth between the liquid  
15 and supercritical states can be performed as many times as  
required. After phase shifting has been completed, the  
cleaning vessel is then depressurized and the treated  
substrate is removed and packaged or treated further.

When cleaning substrates which will be used in the  
20 space environment, the dense fluids may themselves become  
contaminants when subjected to the space environment.  
Therefore, substrates to be used in space are subjected to  
an additional thermal vacuum degassing step after the  
high-pressure dense fluid cleaning process. This step is  
25 shown in FIG. 3 wherein the cleaning vessel is  
depressurized to a vacuum of approximately 1 Torr  
(millimeter of mercury) and a temperature of approximately  
395K (250°F) is applied for a predetermined (i.e.,  
precalculated) period of time in order to completely degas  
30 the hardware and remove any residual gas from the  
hardware. The depressurization of the cleaning vessel  
after the cleaning process has been completed is carried  
out at a rate determined to be safe for the physical  
characteristics, such as tensile strength, of the  
35 substrate.

1 For certain types of substrates, such as polymeric  
materials, internal dense fluid volumes are high upon  
completion of the cleaning process. Accordingly, during  
depressurization, the internal interstitial gas molar  
5 volume changes drastically. The gas effusion rate from  
the polymer is limited depending upon a number of factors,  
such as temperature, gas chemistry, molar volume, and  
polymer chemistry. In order to ease internal stresses  
caused by gas expansion, it is preferred that the fluid  
10 environment in the cleaning vessel be changed through  
dense gas displacement prior to depressurization,  
maintaining relatively constant molar volume. The  
displacement gas is chosen to have a diffusion rate which  
is higher than that of the dense phase gas. This step of  
15 dense gas displacement is shown in FIG. 3 as an optional  
step when polymeric materials are being cleaned. For  
example, if a non-polar dense phase cleaning fluid, such  
as carbon dioxide, has been used to clean a non-polar  
polymer, such as butyl rubber, then a polar fluid, such as  
20 nitrous oxide, should be used to displace the non-polar  
dense fluid prior to depressurization since the polar  
fluid will generally diffuse more readily from the polymer  
pores. Alternatively, dense phase helium may be used to  
displace the dense phase gas cleaning fluid since helium  
25 generally diffuses rapidly from polymers upon  
depressurization.

The present invention may be used to clean a wide  
variety of substrates formed of a variety of materials.  
The process is especially well adapted for cleaning  
30 complex hardware without requiring disassembly. Some  
exemplary cleaning applications include: defluxing of  
soldered connectors, cables and populated circuit boards;  
removal of photoresists from substrates; decontamination  
of cleaning aids such as cotton- or foam-tipped  
35 applicators, wipers, gloves, etc; degreasing of complex

1 hardware; and decontamination of electro-optical, laser  
and spacecraft complex hardware including pumps,  
transformers, rivets, insulation, housings, linear  
bearings, optical bench assemblies, heat pipes, switches,  
5 gaskets, and active metal castings. Contaminant materials  
which may be removed from substrates in accordance with  
the present invention include, but are not limited to,  
oil, grease, lubricants, solder flux residues,  
photoresist, particulates comprising inorganic or organic  
10 materials, adhesive residues, plasticizers, unreacted  
monomers, dyes, or dielectric fluids. Typical substrates  
from which contaminants may be removed by the present  
process include, but are not limited to, substrates formed  
of metal, rubber, plastic, cotton, cellulose, ceramics,  
15 and other organic or inorganic compounds. The substrates  
may have simple or complex configurations and may include  
interstitial spaces which are difficult to clean by other  
known methods. In addition, the substrate may be in the  
form of particulate matter or other finely divided  
20 material. The present invention has application to gross  
cleaning processes such as degreasing, removal of tape  
residues and functional fluid removal, and is also  
especially well-adapted for precision cleaning of complex  
hardware to high levels of cleanliness.

25 In accordance with an alternative embodiment of the  
present invention, a mixture of dense phase gases is  
formulated to have specific solvent properties. For  
example, it is known that dense phase carbon dioxide does  
not hydrogen bond and hence is a poor solvent for  
30 hydrogen-bonding compounds, such as abietic acid, which is  
a common constituent in solder fluxes. We have found by  
calculation that the addition of 10 to 25 percent  
anhydrous ammonia, which is a hydrogen-bonding compound,  
to dry liquid carbon dioxide modifies the solvent  
35 chemistry of the latter to provide for hydrogen bonding

1 without changing the total cohesion energy of the dense  
fluid system significantly. The anhydrous ammonia gas is  
blended with the carbon dioxide gas and compressed to  
liquid-state densities, namely the subcritical or  
5 supercritical state. These dense fluid blends of  $\text{CO}_2$   
and  $\text{NH}_3$  are useful for removing polar compounds, such as  
plasticizers from various substrates. In addition to  
possessing hydrogen-bonding ability, the carbon  
dioxide/ammonia dense fluid blend can dissolve ionic  
10 compounds, and is useful for removing residual ionic flux  
residues from electronic hardware and for regenerating  
activated carbon and ion exchange resins. This particular  
dense phase solvent blend has the added advantage that it  
is environmentally acceptable and can be discharged into  
15 the atmosphere. Similar blends may be made using other  
non-hydrogen-bonding dense fluids, such as blends of  
ammonia and nitrous oxide or ammonia and xenon.

An exemplary system for carrying out the process of  
the present invention is shown diagrammatically in  
20 FIG. 4. The system includes a high pressure cleaning  
chamber or vessel 12. The substrate is placed in the  
chamber 12 on a loading rack as shown in FIG. 5a or  
FIG. 5b. The temperature within the chamber 12 is  
controlled by an internal heater assembly 14 which is  
25 powered by power unit 16 which is used in combination with  
a cooling system (not shown) surrounding the cleaning  
vessel. Coolant is introduced from a coolant reservoir 18  
through coolant line 20 into a coolant jacket or other  
suitable structure (not shown) surrounding the high  
30 pressure vessel 12. The dense fluid used in the cleaning  
process is fed from a gas reservoir 22 into the chamber 12  
through pressure pump 24 and inlet line 25. The system  
may be operated for batch-type cleaning or continuous  
cleaning. For batch-type cleaning, the chamber 12 is  
35 pressurized to the desired level and the temperature of



1 the dense phase gas is adjusted to the starting point for  
the phase shifting sequence, which is either above or  
below the critical temperature of the dense phase gas.  
The vessel is repeatedly pressurized and depressurized  
5 from the original pressure starting point to a pressure  
below the critical pressure. Sequentially, the  
temperature of the vessel is adjusted up or down,  
depending on the types of contaminants, and the  
pressurization/depressurization steps are carried out.  
10 The resulting dense fluid containing contaminants is  
removed from the chamber 12 through exhaust line 26. The  
cleaning vessel may be repressurized with dense phase gas  
and depressurized as many times as required at each  
temperature change. The exhaust line may be connected to  
15 a separator 28 which removes the entrained contaminants  
from the exhaust gas thereby allowing recycling of the  
dense phase gas. Phase shifting by temperature cycling is  
continued and the above-described depressurization and  
repressurizations are performed as required to achieve the  
20 desired level of cleanliness of the substrate.

For continuous cleaning processes, the dense fluid is  
introduced into chamber 12 by pump 24 at the same rate  
that contaminated gas is removed through line 26 in order  
to maintain the pressure in chamber 12 at or above the  
25 critical pressure. This type of process provides  
continual removal of contaminated gas while the phase of  
the dense fluid within chamber 12 is being shifted back  
and forth between liquid and supercritical states through  
temperature cycling.

30 The operation of the exemplary system shown  
schematically in FIG. 4 is controlled by a computer 30  
which utilizes menu-driven advanced process development  
and control (APDC) software. The analog input, such as  
temperature and pressure of the chamber 12, is received by  
35 the computer 30 as represented by arrow 32. The computer

1 provides digital output, as represented by arrow 33 to  
control the various valves, internal heating and cooling  
systems in order to maintain the desired pressure and  
temperature within the chamber 12. The various programs  
5 for the computer will vary depending upon the chemical  
composition and geometric configuration of the particular  
substrate being cleaned, the contaminant(s) being removed,  
the particular dense fluid cleaning gas or gas mixture,  
and the cleaning times needed to produce the required  
10 end-product cleanliness. Normal cleaning times are on the  
order of four hours or less.

Referring to FIGS. 3 and 4, an exemplary cleaning  
process involves initially placing the hardware into the  
cleaning vessel, chamber 12. The chamber 12 is closed and  
15 purged with clean, dry inert gas or the cleaning gas from  
reservoir 22. The temperature of the chamber 12 is then  
adjusted utilizing the internal heating element 14 and  
coolant from reservoir 18 to which is provided externally  
through a jacketing system, in order to provide a  
20 temperature either above or below the critical temperature  
for the cleaning gas or gas mixtures. The chamber 12 is  
then pressurized utilizing pump 24 to a pressure equal to  
or above the critical pressure for the particular dense  
phase gas cleaning fluid. This critical pressure is  
25 generally between about 20 atmospheres (300 pounds per  
square inch or 20.6 kilograms per square centimeter) and  
102 atmospheres (1500 pounds per square inch or 105.4  
kilograms per square centimeter). The processing pressure  
is preferably between 1 and 272 atmospheres (15 and 4000  
30 pounds per square inch or 1.03 and 281.04 kilograms per  
square centimeter) above the critical pressure, depending  
on the breadth of solvent spectrum and associated phase  
shifting range which are required.

Once the pressure in chamber 12 reaches the desired  
35 point above the critical pressure, the pump 24 may be

1 continually operated and exhaust line 26 opened to provide  
continuous flow of dense fluid through the chamber 12  
while maintaining constant pressure. Alternatively, the  
exhaust line 26 may be opened after a sufficient amount of  
5 time at a constant pressure drop to remove contaminants,  
in order to provide for batch processing. For example, a  
pressure drop of 272 atmospheres (4,000 psi) to 102  
atmospheres (1500 psi) over a 20-minute cleaning period  
can be achieved.

10 Phase shifting of the dense fluid between liquid and  
supercritical states is carried out during the cleaning  
process. This phase shifting is achieved by controlled  
ramping of the temperature of the chamber 12 between  
temperatures above the critical temperature of the dense  
15 fluid and temperatures below the critical temperature of  
the dense fluid while maintaining the pressure at or above  
the critical pressure for the dense fluid. When carbon  
dioxide is used as the dense fluid, the temperature of  
chamber 12 is cycled above and below 305K (32° centigrade).

20 FIG. 5 shows two exemplary racks which may be used to  
load and hold the substrates to be cleaned in accordance  
with the present invention. FIG. 5a shows a vertical  
configuration, while FIG. 5b shows a horizontal  
configuration. In FIGS. 5a and 5b, the following elements  
25 are the same as those shown in FIG. 4: chamber or  
pressure vessel 12, gas inlet line 25, and gas outlet  
line(s) 26. A rack 13 with shelves 15 is provided to hold  
the substrates 17 to be treated in accordance with the  
present process. The rack 13 and shelves 15 are made of a  
30 material which is chemically compatible with the dense  
fluids used and sufficiently strong to withstand the  
pressures necessary to carry out the present process.  
Preferred materials for the rack and shelves are stainless  
steel or teflon. The shelves 15 are constructed with  
35 perforations or may be mesh in order to insure the

1 unobstructed flow of the dense fluid and heat transfer  
around the substrates. The rack 13 may have any  
convenient shape, such as cylindrical or rectangular, and  
is configured to be compatible with the particular  
5 pressure vessel used. The vertical configuration of  
FIG. 5a is useful with a pressure vessel of the type shown  
in FIG. 6 or 7 herein, whereas the horizontal  
configuration of FIG. 5b is useful with a pressure vessel  
of the type shown in FIG. 8 herein. As shown in FIG. 5a,  
10 legs or "stand-offs" 21 are provided in order to elevate  
the rack above the sparger carrying the dense phase gas.  
As indicated in FIG. 5b, the rack is held on stand-offs  
(not shown) so that it is located in the upper half of the  
chamber in order to prevent obstruction of fluid flow.  
15 Optionally, in both of the configurations of FIGS. 5a  
and 5b, an additive reservoir 19 may be used in order to  
provide a means of modifying the dense phase gas by  
addition of a selected material, such as methanol or  
hydrogen peroxide. The reservoir 19 comprises a shallow  
20 rectangular or cylindrical tank. The modifier is placed  
in the reservoir 19 when the substrate is loaded into the  
chamber 12. The modifier may be a free-standing liquid or  
it may be contained in a sponge-like absorbent material to  
provide more controlled release. Vapors of the modifier  
25 are released from the liquid into the remainder of the  
chamber 12 during operation of the system. The modifier  
is chosen to enhance or change certain chemical properties  
of the dense phase gas. For example, the addition of  
anhydrous ammonia to xenon provides a mixture that  
30 exhibits hydrogen bonding chemistry, which xenon alone  
does not. Similarly, the modifier may be used to provide  
oxidizing capability or reducing capability in the dense  
phase gas, using liquid modifiers such as ethyl alcohol,  
water, acid, base, or peroxide.

1       An exemplary high pressure cleaning vessel for use in  
practicing a first embodiment of the present process is  
shown at 40 FIG. 6. The vessel or container 40 is  
suitable for use as the high pressure cleaning vessel  
5       shown at 12 in the system depicted in FIG 4. The high  
pressure cleaning vessel 40 includes a cylindrical outer  
shell 42 which is closed at one end with a removable  
enclosure 44. The shell 42 and enclosure 44 are made from  
conventional materials which are chemically compatible  
10       with the dense fluids used and sufficiently strong to  
withstand the pressures necessary to carry out the  
process, such as stainless steel or aluminum. The  
removable enclosure 44 is provided so that materials can  
be easily placed into and removed from the cleaning  
15       zone 46 within outer shell 42.

      An internal heating element 48 is provided for  
temperature control in combination with an external  
cooling jacket 59 surrounding the shell 42. Temperature  
measurements to provide analog input into the computer for  
20       temperature control are provided by thermocouple 50. The  
gas solvent is fed into the cleaning zone 46 through inlet  
52 which is connected to sparger 54. Removal of gas or  
dense fluid from the cleaning zone 46 is accomplished  
through exhaust ports 56 and 58.

25       The cleaning vessel 40 is connected into the system  
shown in FIG. 4 by connecting inlet 52 to inlet line 25,  
connecting heating element 48 to power source 16 using  
power leads 49, and connecting exhaust outlets 56 and 58  
to the outlet line 26. The thermocouple 50 is connected  
30       to the computer 30.

      In accordance with a second embodiment of the present  
invention, the contaminated substrate to be cleaned is  
suspended in a liquid suspension medium, such as deionized  
water, while it is subjected to the phase shifting of the  
35       dense phase gas as previously described. FIG. 7 shows an

1 exemplary cleaning vessel which may be used to practice  
this embodiment of the present invention. The system  
shown in FIG. 7 is operated in the same manner as the  
system shown in FIG. 6 with the exceptions noted below.  
5 In FIG. 7, the following elements are the same as those  
described in previous figures: chamber or cleaning  
vessel 12, substrate 17, gas inlet line 25, and gas  
exhaust line 26. Within the chamber 12, there is an inner  
container 41, which is formed of a chemically resistant  
10 and pressure resistant material, such as stainless steel.  
The container 41 holds the liquid 43, in which the  
substrate 17 is suspended by being placed on a rack (not  
shown). A gas sparger 45 is provided for introducing the  
dense phase gas through the inlet line 25 into the lower  
15 portion of the container 41 and into the liquid 43. The  
phase shifting process is performed as previously  
described herein, and a multiphase cleaning system is  
produced. For example, if deionized water is used as the  
liquid suspension medium and carbon dioxide is used as the  
20 dense phase gas at a temperature greater than 305K and a  
pressure greater than 70 atmospheres, the following  
multiple phases result: (a) supercritical carbon dioxide,  
which removes organic contaminants; (b) deionized water,  
which removes inorganic contaminants; and (c) carbonic  
25 acid formed in situ, which removes inorganic ionic  
contaminants. In addition, during the depressurization  
step as previously described herein, the gas-saturated  
water produces expanding bubbles within the interstices of  
the substrate as well as on the external surfaces of the  
30 substrate. These bubbles aid in dislodging particulate  
contaminants and in "floating" the contaminants away from  
the substrate. The wet supercritical carbon dioxide  
containing the contaminants passes by interphase mass  
transfer from inner container 41 to chamber 12, from which  
35 it is removed through exhaust line 26.

1 After the substrate 17 has been cleaned, it is rinsed  
with clean hot deionized water to remove residual  
contaminants, and is then vacuum dried in an oven at 350K  
for 2 to 4 hours and packaged. Optionally, the substrate  
5 may be first dried with alcohol prior to oven drying.

Other dense phase gases which are suitable for use in  
this second embodiment of the present invention include,  
but are not limited to, xenon and nitrous oxide. In  
addition, the liquid suspension medium may alternatively  
10 contain additives, such as surfactants or ozone, which  
enhance the cleaning process. This embodiment of the  
present invention is particularly well suited for  
precision cleaning of wipers, gloves, cotton-tipped wooden  
applicators, and fabrics.

15 In a third embodiment of the present invention, the  
cleaning action of the dense fluid during phase shifting  
from the liquid to supercritical states may be enhanced by  
applying ultrasonic energy to the cleaning zone. A  
suitable high-pressure cleaning vessel and sonifier are  
20 shown at 60 in FIG. 8. The sonifier 60 includes a  
cylindrical container 62 having removable enclosure 64 at  
one end and ultrasonic transducer 66 at the other end.  
The transducer 66 is connected to a suitable power source  
by way of power leads 68. Such transducers are  
25 commercially available, for example from Delta Sonics of  
Los Angeles, California. Gas solvent feed line 70 is  
provided for introduction of the dense fluid solvent into  
the cleaning zone 74. Exhaust line 72 is provided for  
removal of contaminated dense fluid.

30 The sonifier 60 is operated in the same manner as the  
cleaning vessel shown in FIG. 6 except that a sparger is  
not used to introduce the dense fluid into the cleaning  
vessel and the temperature control of the sonification  
chamber 74 is provided externally as opposed to the  
35 cleaning vessel shown in FIG. 6 which utilizes an internal

1 heating element. The frequency of sonic energy applied to  
the dense fluid during phase shifting in accordance with  
the present invention may be within the range of about 20  
and 80 kilohertz. The frequency may be held constant or,  
5 preferably, may be shifted back and forth over the range  
of 20 to 80 kilohertz. The use of ultrasonic energy  
(sonification) increases cleaning power by aiding in  
dissolving and/or suspending bulky contaminants, such as  
waxes, monomers and oils, in the dense fluid.  
10 Furthermore, operation of the sonic cleaner with high  
frequency sonic bursts agitates the dense phase gas and  
the substrate to promote the breaking of bonds between the  
contaminants and the substrate being cleaned. Use of  
sonification in combination with phase shifting has the  
15 added advantage that the sonification tends to keep the  
chamber walls clean and assists in removal of extracted  
contaminants.

In accordance with a fourth embodiment of the present  
invention, enhancement of the cleaning action of the dense  
20 fluid may be provided by exposing the fluid to high energy  
radiation. The radiation excites certain dense phase gas  
molecules to increase their contaminant-removal  
capability. Such gases include, but are not limited to  
carbon dioxide and oxygen. In addition, radiation within  
25 the range of 185 to 300 nm promotes the cleavage of  
carbon-to-carbon bonds. Thus, organic contaminants are  
photo-decomposed to water, carbon dioxide, and nitrogen.  
These decomposition products are then removed by the dense  
phase gas.

30 An exemplary cleaning vessel for carrying out such  
radiation-enhanced cleaning is shown at 80 in FIG. 9. The  
cleaning vessel 80 includes a container 82 which has a  
removable container cover 84, gas solvent feed port 86  
which has an angled bore to provide for enhanced mixing in  
35 the chamber, and solvent exhaust port 88. The interior



1 surface 90 preferably includes a radiation-reflecting  
liner. The preferred high energy radiation is ultraviolet  
(UV) radiation. The radiation is generated from a  
5 conventional mercury arc lamp 92, generally in the range  
between 180 and 350 nanometers. Xenon flash lamps are  
also suitable. Operation of the lamp may be either high  
energy burst pulsed or continuous. A high pressure quartz  
window 94, which extends deep into the chamber to achieve  
10 a light piping effect, is provided in the container cover  
84 through which radiation is directed into the cleaning  
chamber 96. The cleaning vessel 80 is operated in the  
same manner as the cleaning vessels shown in FIGS. 6 and  
8. Temperature control within the cleaning chamber 96 is  
15 provided by an external heating element and cooling jacket  
(not shown).

The cleaning vessels shown in FIGS. 6-9 are exemplary  
only and other possible cleaning vessel configurations may  
be used in order to carry out the process of the present  
invention. For example, cleaning vessels may be used  
20 wherein both sonification and ultraviolet radiation  
features are incorporated into the vessel. Furthermore, a  
wide variety of external and internal heating and cooling  
elements may be utilized in order to provide the necessary  
temperature control to accomplish phase shifting of the  
25 dense fluid between the liquid and supercritical fluid  
states.

The cleaning vessel shown in FIG. 6 is especially  
useful in creating temperature gradients within the  
cleaning zone 46. The internally located heating element  
30 48 in combination with an externally mounted cooling  
jacket or chamber makes it possible to create a  
temperature gradient within the cleaning chamber 46 when  
the flow rate and pressure of dense fluid is constant.  
Such a thermal gradient in which the temperature of the  
35 dense fluid decreases moving from the center toward the

1 container walls, provides thermal diffusion of certain  
contaminants away from the substrate which is usually  
located centrally within the chamber. This thermal  
gradient also provides "solvent zones", that is a range of  
5 distinct solvents favoring certain contaminants or  
contaminant groups, which enhances the contaminant removal  
process.

In accordance with a fifth embodiment of the present  
invention, the dense fluid may comprise a mixture of a  
10 first dense phase fluid which chemically reacts with the  
contaminant to thereby facilitate removal of the  
contaminant, and a second dense phase fluid which serves  
as a carrier for the first dense phase fluid. For  
example, supercritical ozone or "superozone" is a highly  
15 reactive supercritical fluid/oxidant at temperatures  
greater than or equal to 270K and pressures greater than  
or equal to 70 atmospheres. The ozone may be generated  
external to the cleaning vessel, such as that shown in  
FIG. 6, mixed with a carrier gas, and introduced into the  
20 cleaning zone 46 through inlet 52. Known methods of  
forming ozone from oxygen by silent direct current  
discharge in air, water, or liquid oxygen and ultraviolet  
light exposure of air, as described, for example, in the  
publication entitled "UV/Ozone Cleaning for Organics  
25 Removal on Silicon Wafers," by L. Zaronte and R. Chiu,  
Paper No. 470-19, SPIE 1984 Microlithography Conference,  
March 1984, Santa Clara, California; and in the  
publication entitled "Investigation into the Chemistry of  
the UV-Ozone Purification Process," U.S. Department of  
30 Commerce, National Science Foundation, Washington D.C.,  
January 1979 may be used. Optionally, the ozone may be  
generated in situ within a cleaning vessel of the type  
shown in FIG. 9 in which the quartz window 94 is replaced  
with a quartz light pipe array which pipes the ozone-

1 producing ultraviolet light deep into the dense phase gas  
mixture. Oxygen, optionally blended with a carrier gas  
such as carbon dioxide, xenon, argon, krypton, or ammonia,  
is introduced into chamber 80 through gas solvent feed  
5 port 86. If no carrier gas is used in the input gas,  
excess oxygen serves as the carrier for the newly formed  
ozone. In practice, the substrate is placed in the  
chamber 80 and the system is operated as described for the  
system of FIG. 9. The mercury lamps 92 are activated to  
10 produce 185 nanometer radiation which strikes the oxygen  
gas ( $O_2$ ) and converts it to ozone ( $O_3$ ). After  
adjustment of the system pressure and temperature to form  
a dense phase gas, the superozone is transported to the  
substrate surface as a dense phase gas oxidant in the  
15 secondary dense fluid (i.e., dense phase carbon dioxide,  
argon, oxygen, or krypton).

Superozone has both gas-like and liquid-like chemical  
and physical properties, which produces increased  
permeation of this dense phase gas into porous structures  
20 or organic solids and films and more effective contaminant  
removal. In addition, superozone is both a polar solvent  
and an oxidant under supercritical conditions and  
consequently is able to dissolve into organic surface  
films or bulky compounds and oxidatively destroy them.  
25 Oxidation by-products and solubilized contaminants are  
carried away during depressurization operations previously  
described. The use of superozone has the added advantage  
that no hazardous by-products or waste are generated.  
This embodiment of the present invention using superozone  
30 is particularly useful for deep sterilization of various  
materials, destroying unreacted compounds from  
elastomeric/resinous materials, in-situ destruction of  
organic hazardous wastes, precision cleaning of optical  
surfaces; preparation of surfaces for bonding processes;

1 surface/subsurface etching of substrate surfaces, and  
reducing volatile organic compound levels in substrates,  
to produce materials and structures which meet NASA  
requirements for space applications.

5 Other materials which chemically react with the target  
contaminants may alternatively be used in this third  
embodiment of the present invention. For example,  
hydrogen peroxide can be used in place of ozone to provide  
an oxidant to react with the target contaminants.

10 Moreover, other types or reactions besides oxidation can  
be effected in accordance with the present invention. For  
example, a material, such as ammonia, which can be  
photodissociated to form hydrogen species, can chemically  
reduce the target contaminants. A material, such as  
15 fluorine gas, which can be photodissociated to form  
fluorine, or other halogen radicals, can react with target  
contaminants.

Examples of practice of the present invention are as  
follows.

20

#### EXAMPLE 1

This example illustrates the use of one embodiment of  
the present invention to remove a variety of contaminants  
25 from a cotton-tipped wooden applicator in preparation for  
using the applicator as a precision cleaning aid. The  
contaminants comprised wood oils, adhesive residues,  
particulate matter, cellulose, lignin, triglycerides,  
resins and gums with which the applicator had become  
30 contaminated during manufacture or through prior use in  
precision cleaning, or by their natural composition.

The dense phase gas used in practicing the present  
process comprised 90 percent by volume carbon dioxide and  
10 percent by volume nitrous oxide. The critical  
35 temperature for carbon dioxide is approximately 305K and

1 the critical pressure is approximately 72 atmospheres.  
The critical temperature of nitrous oxide is 309K and the  
critical pressure is approximately 72 atmospheres.

5 The flowchart of FIG. 3 and the cleaning vessel of  
FIG. 6 were used as previously described herein. The  
contaminated substrate, namely the cotton-tipped wooden  
applicator, was placed on a rack and then in the cleaning  
vessel 12, and the vessel was purged with inert gas. The  
10 temperature of the vessel was adjusted to approximately  
320K. Next, the cleaning chamber was pressurized with the  
carbon dioxide-nitrous oxide mixture to about  
275 atmospheres. One cycle of phase shifting was carried  
out by incrementally varying (ramping) the temperature of  
the gas mixture from 320K to approximately 300K, which  
15 changed the gas solvent cohesive energy from approximately  
 $12 \text{ MPa}^{1/2}$  to  $22 \text{ MPa}^{1/2}$  and then incrementally increasing  
the temperature from 300K to 320K, which changed the gas  
solvent cohesive energy content from approximately  $22 \text{ MPa}^{1/2}$   
to  $12 \text{ MPa}^{1/2}$ . The gas mixture was allowed to contact the  
20 contaminated substrate after each temperature change  
(change in solvency) for 1 to 3 minutes prior to beginning  
batch or continuous cleaning operations. Phase shifting  
was carried out for approximately 30 minutes at a rate of  
1 cycle every 5 minutes for continuous cleaning operations,  
25 and optionally for approximately 60 minutes at a rate of  
1 cycle every 15 minutes for batch cleaning operations.  
The cleaned substrate typically exhibited a weight loss of  
2 to 4%, and solvent leachate tests showed less than  
1 milligram of extractable residue per applicator. The  
30 cleaned substrate was packaged and sealed.

As previously discussed, this phase shifting process  
creates a "solvent spectrum" which overlaps the cohesive  
energy ranges for the contaminants and therefore provides  
a suitable solvent for each of the contaminants present in  
35 the cotton-tipped wooden applicator.

1       The above-described procedure utilizing carbon dioxide  
and nitrous oxide as the dense phase gas can be extended  
to other types of substrates containing a wide range of  
contaminants, including foam-tipped plastic applicators,  
5       wiping cloths, cotton balls and gloves.

### EXAMPLE 2

10       This example illustrates the use of the process of the  
present invention in order to clean a substrate to meet  
NASA outgassing requirements. The substrate comprised  
soldered pin connectors and the contaminants were solder  
flux residues, particulate matter, skin, oils,  
plasticizers, and potential outgassing contaminants.

15       The general procedure described in Example 1 was  
followed except that 100 percent carbon dioxide was used  
as the dense phase gas. The phase shift temperature range  
was approximately 310K to 298K at a pressure of  
approximately 200 atmospheres. Phase shifting was carried  
20       out for approximately 30 minutes at a rate of 1 cycle  
every 10 minutes. Following gas solvent cleaning, the  
vessel temperature was raised to 395K (250°F) and a  
vacuum of 1 Torr was applied for 1 hour to remove residual  
gas. The cleaned substrate exhibited no signs of visible  
25       contamination in the pin sockets, and standard  
thermal-vacuum outgassing tests in accordance with ASTM  
Standard E595 showed a total mass loss (TML) of less than  
1.0% and a volatile condensable material (VCM) content of  
less than 0.1% for the entire assembly, which meets NASA  
30       outgassing requirements. The cleaned substrate was  
packaged and sealed as usual for subsequent operations.

1

EXAMPLE 3

5 The example illustrates the use of the process of the present invention to remove unreacted oils, colorants and fillers from fluorosilicone interfacial seals in order to improve insulation resistance (dielectric properties).

10 The general procedure described in Example 1 was followed except that 100 percent carbon dioxide was used as the dense phase gas. The phase shift temperature range was approximately 300K to 320K at a pressure of approximately 170 atmospheres. Phase shifting from the liquid state to the supercritical state was employed in order to first swell the bulk polymer (i.e., the fluorosilicone) in liquid CO<sub>2</sub> and then remove  
15 interstitial contaminants during phase shift operations. Phase shifting was carried out for approximately 30 minutes at a rate of 1 cycle every 10 minutes. Following cleaning operations, the material was thermal-vacuum degassed and packaged. The cleaned substrates exhibited  
20 weight losses of 4% to 10%, and the column to column insulation resistance was improved 15-fold.

EXAMPLE 4

25 This example illustrates the use of the process of the present invention to remove surface contaminants, including solder flux residues, finger oils, and particulate matter, from ferrite cores prior to encapsulation in order to eliminate possible high-voltage  
30 interfacial dielectric breakdown.

The general procedure described in Example 1 was followed except that the dense phase gas comprised  
35 75 percent by volume dry carbon dioxide and 25 percent by volume anhydrous ammonia. The phase shift temperature range was approximately 375K to 298K at a pressure of

1 about 240 atmospheres. Ammonia has a critical pressure of  
approximately 112 atmospheres and a critical temperature  
of approximately 405K. During the phase shifting  
operation, which was typically 1 cycle every 10 minutes  
5 for 45 minutes, the substrate was bathed in a two-phase  
system (supercritical carbon dioxide/liquid ammonia) at  
temperatures above 305K and a binary solvent blend (liquid  
carbon dioxide-ammonia) at temperatures below 305K.  
Following cleaning operations, the substrate was packaged  
10 and sealed. The cleaned substrate exhibited visibly clean  
surfaces, and surface contamination tests showed less than  
15 milligrams of ionic contaminants per square inch of  
surface area.

The above-described cleaning operation utilizing dense  
15 phase carbon dioxide and dense phase ammonia can be  
extended to other types of substrates containing a wide  
range of ionic/nonionic and organic/inorganic  
contaminants, including printed wiring boards, electronic  
connectors, spacecraft insulating blankets, and ceramic  
20 daughter boards.

#### EXAMPLE 5

25 This example illustrates the use of the process of the  
present invention to remove machining oils, finger oils,  
and particulate matter from optical benches (active metal  
casting) to meet NASA outgassing requirements. The  
contaminants were removed from internal cavities as well  
as the external surfaces of the substrate.

30 The general procedure described in Example 1 was  
followed except that 100 percent carbon dioxide was used  
as the dense phase gas. The phase shift temperature range  
was 305K to 325K at about 340 atmospheres. Phase shifting  
was carried out at a rate of 1 cycle every 10 minutes.  
35 Following cleaning operations, the substrate was



1 thermal-vacuum degassed at 375K and 1 Torr (millimeter of  
mercury) for 30 minutes. The cleaned substrate was  
packaged and sealed. The cleaned substrate exhibited a  
TML of less than 1.0% and a VCM of less than 0.1%.

5 The above-described cleaning operation utilizing dense  
phase carbon dioxide can be extended to other types of  
substrates containing a wide range of contaminants  
including spacecraft fasteners, linear bearings, and heat  
pipes.

10

#### EXAMPLE 6

This example illustrates the use of the process of the  
present invention to remove non-aqueous and semi-aqueous  
photoresist from printed wiring boards in order to prepare  
the boards for subsequent processing steps.

15 The general procedure described in Example 1 was  
followed except that the dense phase gas comprised xenon.  
Xenon has a critical pressure of approximately  
20 57 atmospheres and a critical temperature of approximately  
290K. Dense phase xenon was used at approximately  
140 atmospheres and a phase shift temperature range of  
285K to 300K was used to penetrate, swell, and separate  
the photoresist from the substrate. The phase shifting  
25 process was carried out as many times as necessary to  
effect adequate separation of the photoresist from the  
substrate. Optionally, other gases, for example ammonia,  
may be added to xenon to produce appropriate blends for  
various types of photoresists with varying cohesive  
30 energies and properties.

Thus, from the previous examples, it may be seen that  
the present invention provides an effective method for  
removing two or more contaminants from a given substrate  
in a single process. The types of contaminants removed in  
35 accordance with the present invention may have a wide

1 variety of compositions and the substrates may vary widely  
in chemical composition and physical configuration.

5 The process of the present invention has wide  
application to the preparation of structures and materials  
for both terrestrial and space environments including  
gaskets, insulators, cables, metal castings, heat pipes,  
bearings and rivets. The particular cleaning fluid and  
phase shifting conditions utilized will vary depending  
upon the particular contaminants desired to be removed.  
10 The process is also especially well-suited for removing  
greases and oils from both internal and external surfaces  
of complex hardware.

15 Having thus described exemplary embodiments of the  
present invention, it should be noted by those skilled in  
the art that the within disclosures are exemplary only and  
that various other alternatives, adaptations, and  
modifications may be made within the scope of the present  
invention. Accordingly, the present invention is not  
limited to the specific embodiments as illustrated herein,  
20 but is only limited by the following claims.

CLAIMSWhat is Claimed is:

- 1        1. A process for removing two or more contaminants  
from a chosen substrate comprising the steps of:
  - a) placing said substrate containing said  
contaminants in a cleaning vessel;
  - 5        b) contacting said substrate containing said  
contaminants with a chosen dense phase gas at a pressure  
equal to or above the critical pressure of said dense  
phase gas; and
  - 10        c) shifting the phase of said dense phase gas between  
the liquid state and the supercritical state by varying  
the temperature of said dense phase gas in a series of  
steps between a temperature above the critical temperature  
of said dense phase gas and a temperature below said  
critical temperature, maintaining said temperature at the  
15        completion of each said step for a predetermined period of  
time, and maintaining contact between said dense phase gas  
and said substrate containing said contaminants for said  
predetermined period of time at each said step wherein a  
solvent spectrum of said dense phase gas is provided to  
20        thereby remove said two or more contaminants from said  
substrate.
- 1        2. The process as set forth in Claim 1 wherein said  
varying said temperature comprises starting at a first  
temperature below said critical temperature, increasing  
said temperature to a second temperature above said  
5        critical temperature, and then decreasing said temperature  
to said first temperature.
- 1        3. The process as set forth in Claim 1 wherein said  
varying said temperature comprises starting at a first

temperature above said critical temperature, decreasing said temperature to a second temperature below said critical temperature, and then increasing said temperature to said first temperature.

1           4. The process as set forth in Claim 2 or 3 wherein said varying is performed more than one time.

1           5. The process as set forth in Claim 1 wherein said temperature is varied above said critical temperature by about 5 to 100K.

1           6. The process as set forth in Claim 1 wherein said temperature is varied below said critical temperature by about 5 to 25K.

1           7. The process as set forth in Claim 5 or 6 wherein each said step comprises a change in temperature of about 5 to 10K.

1           8. The process as set forth in Claim 5 or 6 wherein said predetermined period of time is within the range of about 5 to 30 minutes.

1           9. The process as set forth in Claim 1 wherein said dense phase gas is selected from the group consisting of carbon dioxide, nitrous oxide, ammonia, helium, krypton, argon, methane, ethane, propane, butane, pentane, hexane, ethylene, propylene, tetrafluoromethane, chlorodifluoromethane, sulfur hexafluoride, perfluoropropane, and mixtures thereof.

1           10. The process as set forth in Claim 9 wherein said dense phase gas is selected from the group consisting of a mixture of carbon dioxide and nitrous oxide and a mixture of dry carbon dioxide and anhydrous ammonia.

1        11. The process as set forth in Claim 1 wherein said  
contaminant is selected from the group consisting of oil,  
grease, lubricant, solder flux residue, photoresist,  
adhesive residue, plasticizer, unreacted monomer,  
5 inorganic particulates, and organic particulates.

1        12. The process as set forth in Claim 1 wherein said  
dense phase gas containing said contaminants is  
continually removed from said cleaning vessel and replaced  
with additional dense phase gas in an amount sufficient to  
5 maintain the pressure in said cleaning vessel at or above  
said critical pressure.

1        13. The process as set forth in Claim 1 further  
including after step "c", subjecting said substrate to  
thermal vacuum degassing to thereby remove residual dense  
phase gas from said substrate.

1        14. The process as set forth in Claim 1 further  
including after step "c", displacing said dense phase gas  
with a chosen gas having a relatively high diffusion rate  
and then depressurizing said cleaning vessel.

1        15. The process as set forth in Claim 1 wherein said  
substrate is suspended in a liquid solvent to thereby  
enhance removal of said contaminants from said substrate.

1        16. The process as set forth in Claim 1 wherein said  
dense phase gas is exposed to ultraviolet radiation to  
thereby enhance removal of said contaminants from said  
substrate.

1        17. The process as set forth in Claim 1 wherein said  
dense phase gas and said substrate containing said  
contaminants are exposed to ultrasonic energy to thereby  
enhance removal of said contaminants from said substrate.

1        18. The process as set forth in Claim 1 wherein said  
dense phase gas and said substrate containing said  
contaminants are exposed to ultraviolet radiation and  
5        ultrasonic energy to thereby enhance removal of said  
contaminants from said substrate.

1        19. The process as set forth in Claim 1 wherein said  
dense phase gas comprises a mixture of a first dense phase  
gas capable of chemically reacting with said contaminants  
to thereby enhance the removal of said contaminants, and a  
5        second dense phase gas as a carrier for said first dense  
phase gas.

1        20. The process as set forth in Claim 19 wherein said  
first dense phase gas comprises ozone.

1        21. The process as set forth in Claim 20 wherein said  
ozone is generated in situ when said dense phase gas is  
contacted with said substrate.

1        22. The process as set forth in Claim 1 wherein said  
shifting of said phase of said dense phase gas is  
accomplished under computer control.

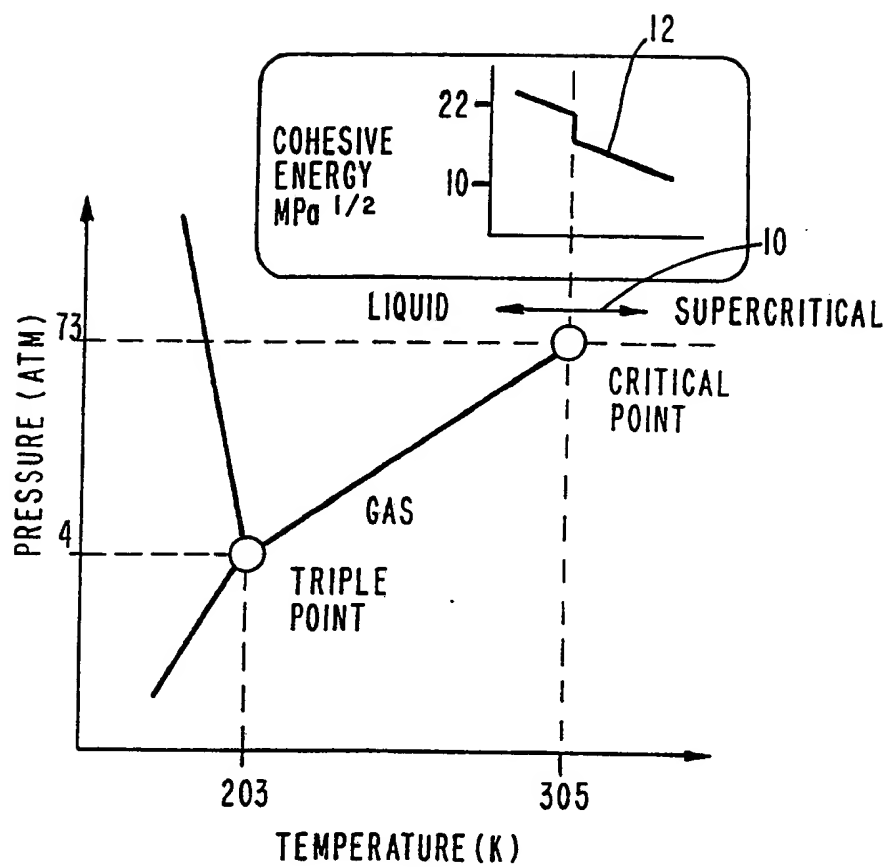


Fig. 1.

Fig. 2.

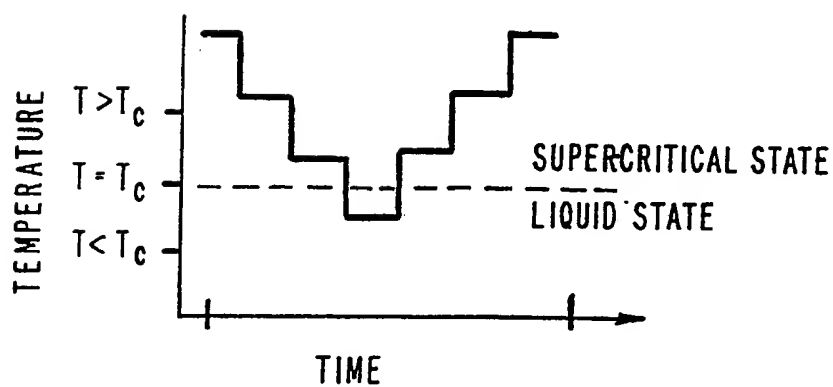
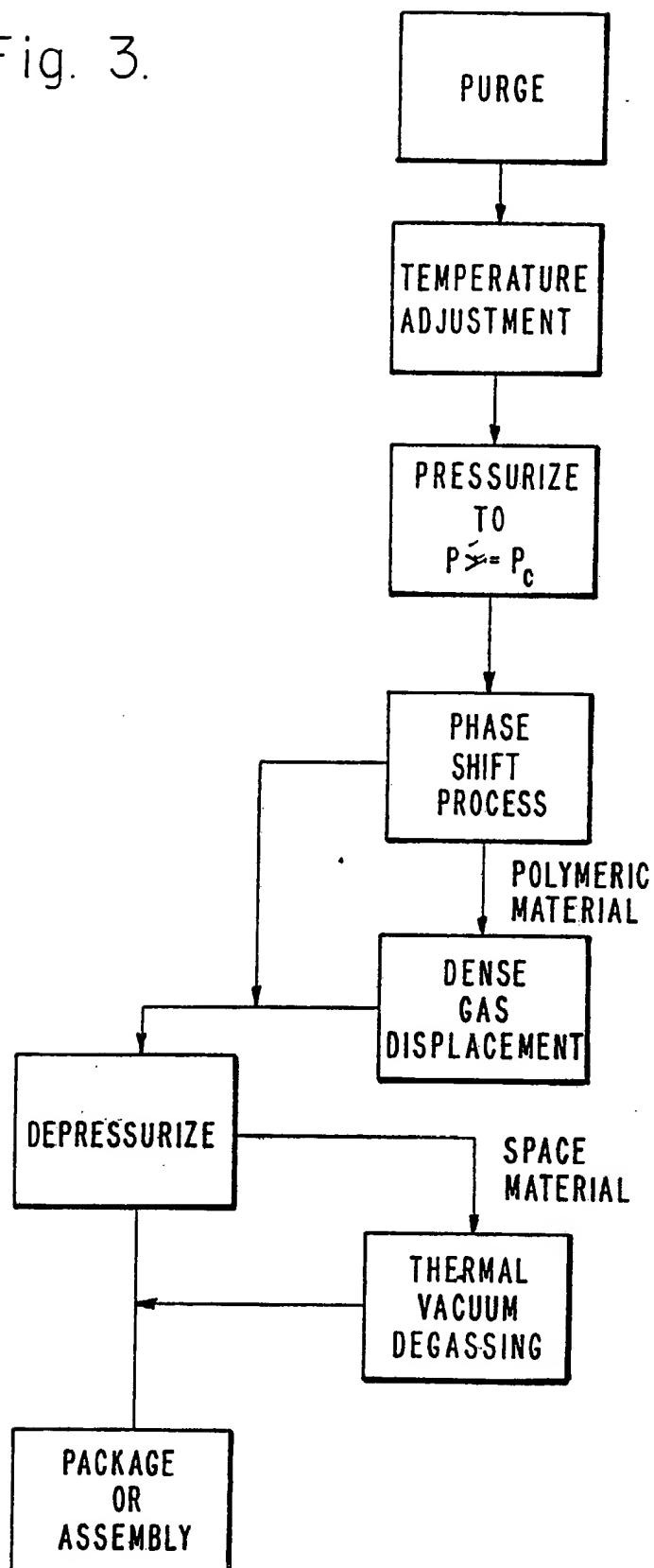


Fig. 3.





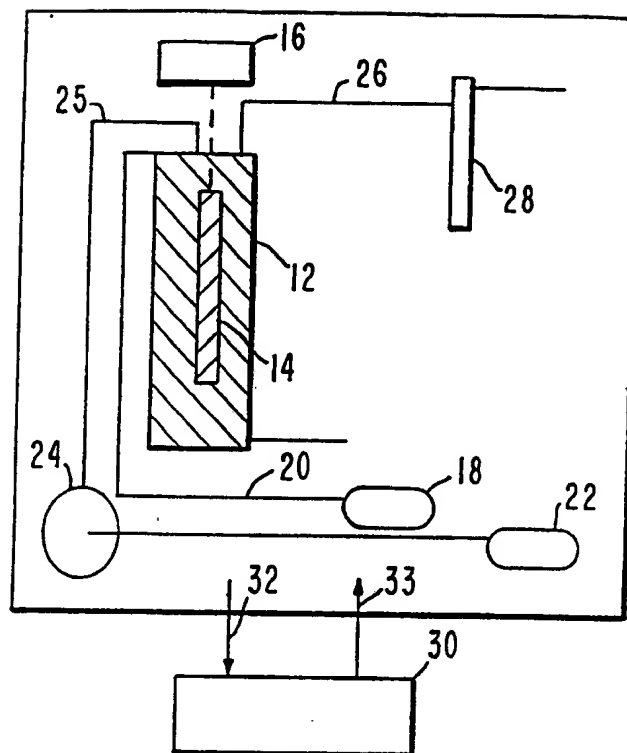


Fig. 4.

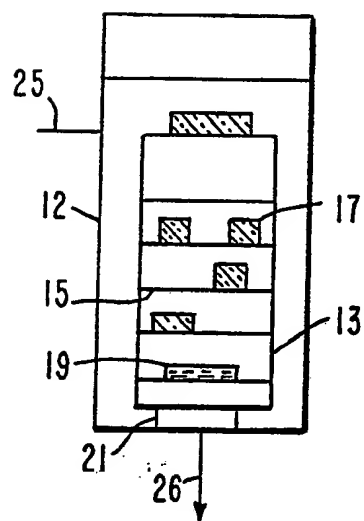


Fig. 5a.

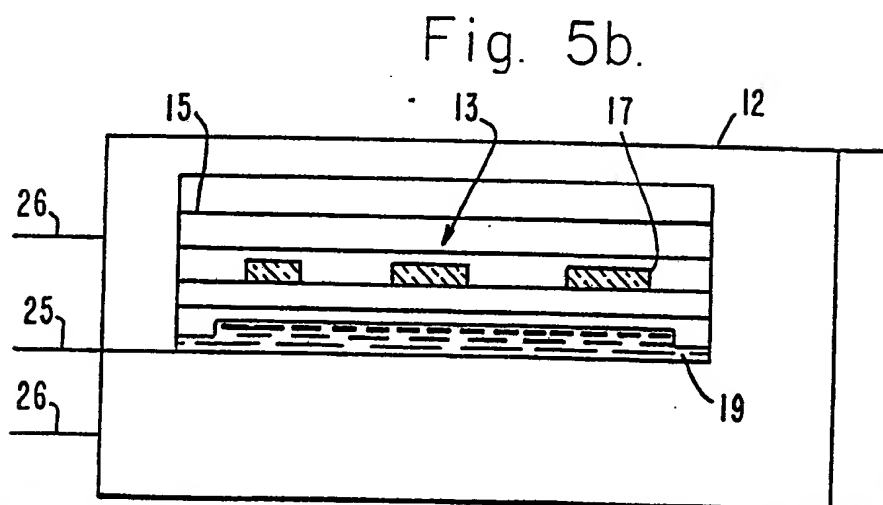


Fig. 5b.

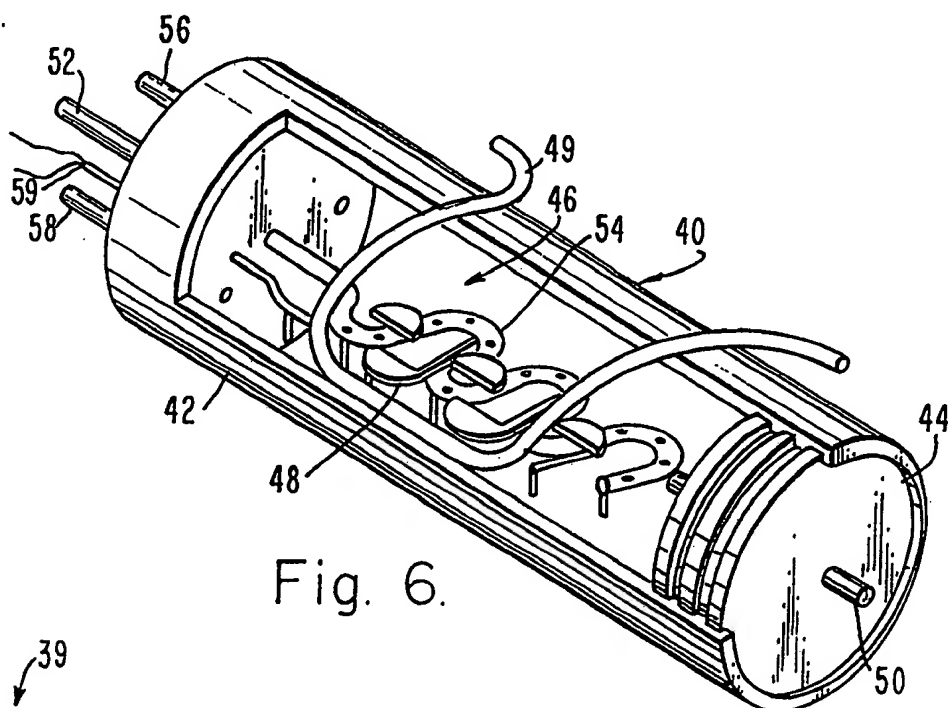


Fig. 6.

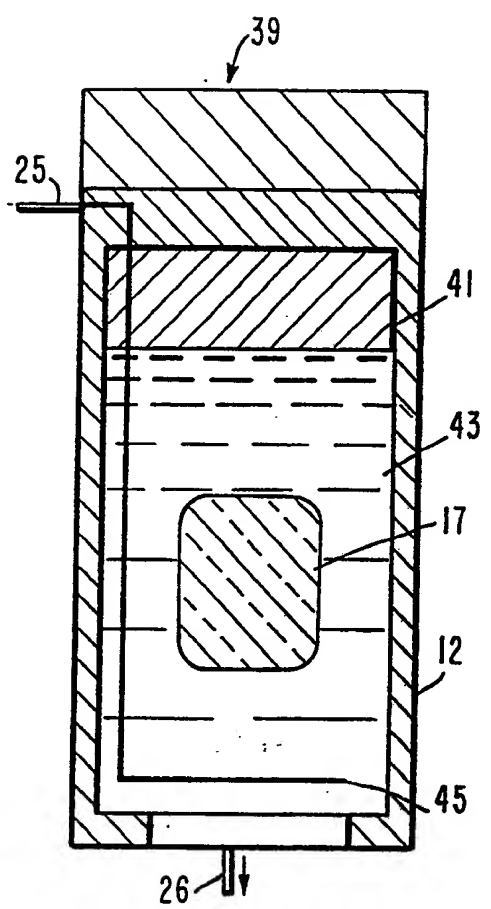


Fig. 7

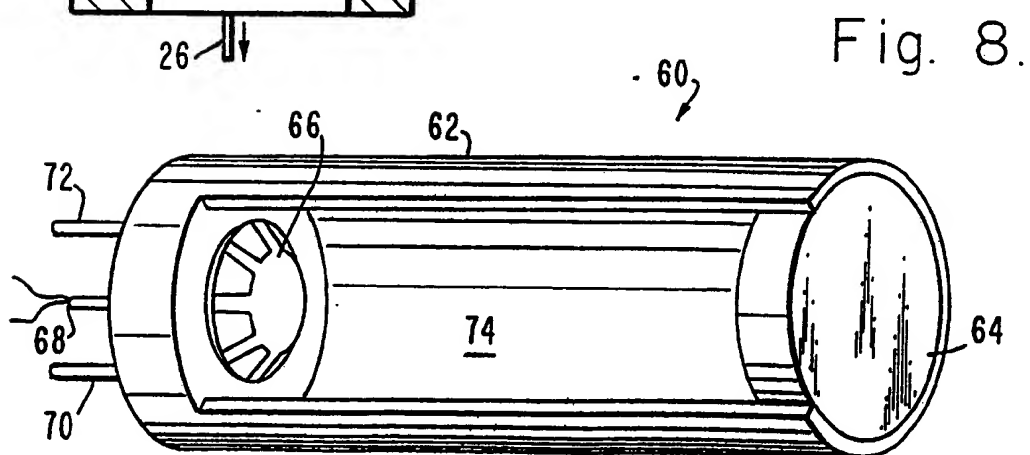


Fig. 8.

Fig. 9a.

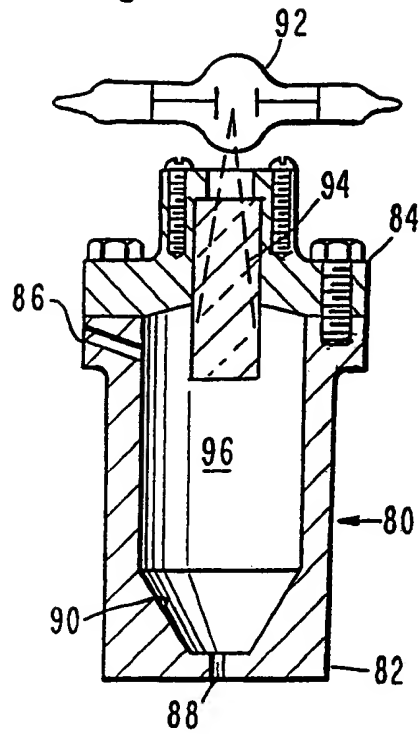
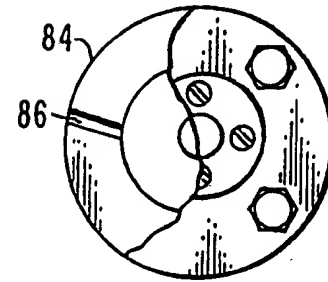


Fig. 9b



# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 89/04674

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC<sup>5</sup>: B 08 B 7/00, C 23 G 5/00

## II. FIELDS SEARCHED

Minimum Documentation Searched <sup>7</sup>

Classification System

Classification Symbols

IPC<sup>5</sup> : B 08 B 7/00, C 23 G 5/00

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>

## III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>

Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
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A	WO, A, 8402291 (HUGHES AIRCRAFT COMPANY) 21 June 1984 see claims	1
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A	Patents Abstracts of Japan, volume 10, no. 35 (E-380)(2092), 12 February 1986 & JP, A, 60192333 (HITACHI SEISAKUSHO K.K.) 30 September 1985 see the abstract	1
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A	US, A, 4576837 (G. TARANCON) 18 March 1986	
--		

A	DE, A, 2544116 (A.D. LITTLE) 8 April 1976 & US, A, 4124528 cited in the application	
-----		

### \* Special categories of cited documents: <sup>14</sup>

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

12th April 1990

Date of Mailing of this International Search Report

22.05.90

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

W. F. S.

M. P. 23

ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.

US 8904674  
SA 32339

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 14/05/90. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US-A- 4576837	18-03-86	None	
DE-A- 2544116	08-04-76	US-A- 4124528	07-11-78
		CA-A- 1064891	23-10-79
		GB-A- 1522352	23-08-78
		JP-A, B, C51061484	28-05-76
		US-A- 4061566	06-12-77